

Claims

What is claimed is:

1. A method for bonding a first substrate to a second substrate comprising:

- 5 (a) providing a metathesis catalyst at the first substrate to form a treated first substrate;
- (b) providing a metathesizable mixture containing 0.5 – 20 mol% of a metathesizable crosslinker dissolved in a principal metathesizable material, on said second substrate or as a component of the second substrate; and
- 10 (c) joining said treated first substrate with said second substrate with the metathesizable material there between whereby the metathesizable material initiates a metathesis reaction to form a crosslinked polymer bonding the first substrate to the second substrate.

15 2. A method according to claim 1 wherein at least one of the substrates comprises an elastomeric material.

3. A method according to claim 2 wherein the elastomeric material is a thermoplastic elastomer.

20 4. A method according to claim 1 wherein one of the first or second substrates comprises a metallic material and the other first or second substrate comprises an elastomeric material.

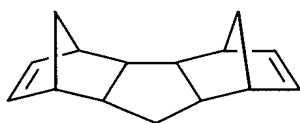
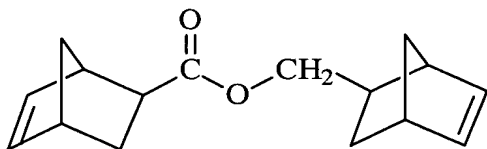
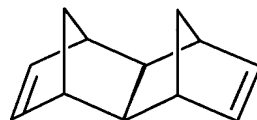
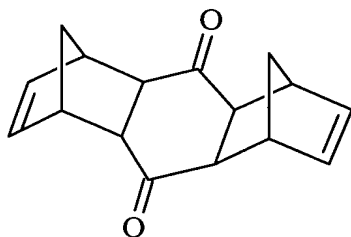
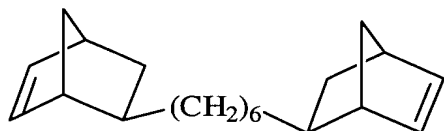
25 5. A method according to claim 4 wherein the metallic material comprises steel and the elastomeric material is selected from natural rubber, polychloroprene, polybutadiene, polyisoprene, styrene-butadiene copolymer rubber, acrylonitrile-butadiene copolymer rubber, ethylene-propylene copolymer rubber, ethylene-propylene-diene terpolymer rubber, butyl rubber, brominated butyl rubber, alkylated chlorosulfonated
30 polyethylene rubber, hydrogenated nitrile rubber, silicone rubber, fluorosilicone rubber, poly(n-butyl acrylate), thermoplastic elastomer and mixtures thereof.

6. A method according to claim 1 wherein the first substrate comprises a tire carcass and the second substrate comprises a tire tread.

7. A method according to claim 1 wherein step (b) comprises applying the metathesizable mixture to the second substrate surface and step (c) comprises contacting the catalyst on the first substrate surface and the treated second substrate surface.

8. A method according to claim 1 wherein at least one of the substrates is substantially cured elastomeric material.

9. A method according to claim 1 wherein the metathesizable mixture comprises (a) and (b) wherein (a) is selected from the group consisting of norbornene, methylenenorbornene, ethylenenorbornene, norbornadiene, dicyclopentadiene, cyclooctene, cyclohexenyl norbornene and (b) is selected from the group consisting of



10. A method according to claim 1 wherein step (c) is conducted at ambient temperature.

5 11. A method according to claim 1 wherein steps (a)-(c) occur at room temperature.

12. A method according to claim 6 wherein the bonding in step (c) occurs within one hour.

10 13. A method according to claim 1 wherein step (a) comprises applying a catalyst onto the first substrate surface.

15 14. A method according to claim 13 wherein the metathesis catalyst is dissolved or mixed into a liquid carrier fluid and applied to the first substrate and the liquid or carrier is removed prior to step (c).

15. A method according to claim 13 wherein the metathesis catalyst is included as a component in a multi-component composition.

20 16. A method according to claim 1 wherein the metathesis catalyst is included as a component of the first substrate.

25 17. A method according to claim 7 wherein the principal metathesizable material is in the form of a liquid, paste or meltable solid.

18. A method according to claim 7 wherein the principal metathesizable material is included as a component in a multi-component composition.

30 19. A method according to claim 1 wherein the principal metathesizable material is included as a component of the second substrate.

20. A method for bonding a metallic substrate to an elastomeric substrate comprising:

- (a) applying a solid metathesis catalyst to a portion of the metallic substrate surface forming a treated metallic substrate;
- (b) applying a metathesizable mixture comprising a metathesizable crosslinking monomer dissolved in a principal metathesizable material to the elastomeric substrate surface; and
- (c) bringing the metallic substrate surface and the elastomeric substrate surface together to contact the catalyst and the metathesizable material, thereby initiating a metathesis polymerization and crosslinking reaction.

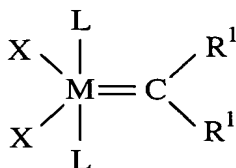
21. A method according to claim 20 wherein step (c) occurs at ambient temperature.

22. A method according to claim 20 wherein the elastomeric substrate is a substantially cured elastomeric material.

23. A method according to claim 1 wherein the metathesis catalyst is selected from at least one of a rhenium compound, ruthenium compound, osmium compound, molybdenum compound, tungsten compound, titanium compound, niobium compound, iridium compound and $MgCl_2$.

24. A method according to claim 23 wherein the metathesis catalyst is selected from a ruthenium compound, a molybdenum compound, iridium compound and an osmium compound.

25. A method according to claim 24 wherein the metathesis catalyst has a structure represented by



wherein M is Os, Ru or Ir; each R¹ is the same or different and is H, alkenyl, alkynyl, alkyl, aryl, alkaryl, aralkyl, carboxylate, alkoxy, alkenylalkoxy, alkenylaryl, alkynylalkoxy, aryloxy, alkoxy carbonyl, alkylthio, alkylsulfonyl or alkylsulfinyl; X is the same or different and is an anionic ligand group; and L is the same or different and is a neutral electron donor group.

26. A method according to claim 25 wherein X is Cl, Br, I, F, CN, SCN, or N₃; L is Q(R²)_a wherein Q is P, As, Sb or N; R² is H, cycloalkyl, alkyl, aryl, alkoxy, arylate or a heterocyclic ring; and a is 1, 2 or 3; M is Ru; and R¹ is H, phenyl, -CH=C(phenyl)₂, -CH=C(CH₃)₂ or -C(CH₃)₂(phenyl).

27. A method according to claim 26 wherein the metathesis catalyst is a phosphine-substituted ruthenium carbene.

28. A method according to claim 27 wherein the catalyst is bis(tricyclohexylphosphine)benzylidene ruthenium (IV) dichloride.

29. A method according to claim 1 wherein the metathesis catalyst is stable in the presence of moisture and oxygen and can initiate polymerization of the metathesizable material upon contact at room temperature.

30. A method according to claim 1 wherein the principal metathesizable material includes at least one reactive unsaturated metathesizable functional group.

31. A method according to claim 30 wherein the principal metathesizable material comprises an olefin.

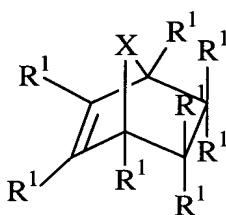
32. A method according to claim 31 wherein the principal metathesizable material is selected from ethene, α -alkene, acyclic alkene, acyclic diene, acetylene, cyclic alkene, cyclic polyene and mixtures thereof.

33. A method according to claim 32 wherein the principal metathesizable material comprises a cycloolefin.

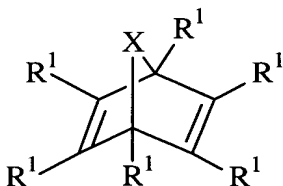
34. A method according to claim 33 wherein the principal metathesizable material is a monomer or oligomer selected from norbornene, cycloalkene, cycloalkadiene, cycloalkatriene, cycloalkatetraene, aromatic-containing cycloolefin and mixtures thereof.

35. A method according to claim 34 wherein the metathesizable material is a norbornene monomer or oligomer.

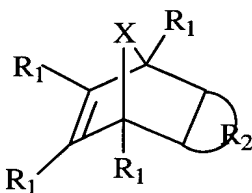
36. A method according to claim 35 wherein the norbornene has a structure represented by



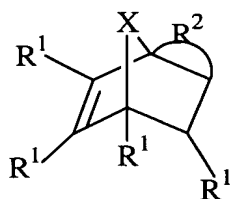
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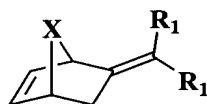
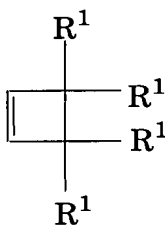
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wherein X is CH₂, CHR³, C(R³)₂, O, S, N-R³, P-R³, O=P-R³, Si(R³)₂, B-R³ or As-R³; each R¹ is independently H, CH₂, alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkaryl, aralkyl, halogen, halogenated alkyl, halogenated alkenyl, alkoxy, oxyalkyl, carboxyl, carbonyl, amido, (meth)acrylate-containing group, anhydride-containing group, thioalkoxy, sulfoxide, nitro, hydroxy, keto, carbamato, sulfonyl, sulfinyl, carboxylate, silanyl, cyano or imido; R² is a fused aromatic, aliphatic or heterocyclic or polycyclic ring; and R³ is alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkaryl, aralkyl or alkoxy..

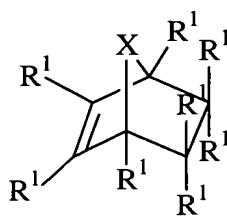
37. A method according to claim 36 wherein the principal metathesizable material comprises ethyldenenorbornene monomer or oligomer.

38. A method according to claim 1 wherein the principal metathesizable material comprises liquid ethylidenenorbornene monomer.

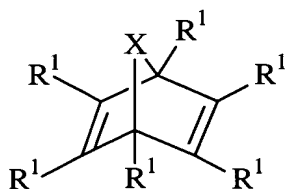
39. A method according to claim 1 wherein the catalyst is applied in an aqueous solution or mixture and the metathesizable material is applied in the form of a liquid that is substantially 100 percent reactive.

40. A method according to claim 1 wherein the method is substantially free of the use of volatile organic solvents.

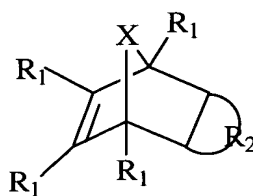
41. A method according to claim 20 wherein the principal metathesizable material comprises norbornene monomer or oligomer having a structure represented by



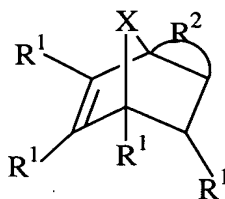
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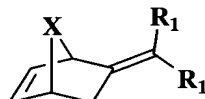
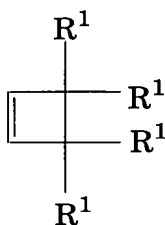
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or



or



wherein X is CH_2 , CHR^3 , $\text{C}(\text{R}^3)_2$, O, S, N-R^3 , P-R^3 , O=P-R^3 , $\text{Si}(\text{R}^3)_2$, B-R^3 or As-R^3 ; each R^1 is independently H, CH_2 , alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkaryl, aralkyl, halogen, halogenated alkyl, halogenated alkenyl, alkoxy, oxyalkyl, carboxyl, carbonyl, amido, (meth)acrylate-containing group, anhydride-containing group, thioalkoxy, sulfoxide, nitro, hydroxy, keto, carbamato, sulfonyl, sulfinyl, carboxylate, silanyl, cyano or imido; R^2 is a fused aromatic, aliphatic or heterocyclic or polycyclic ring; and R^3 is alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkaryl, aralkyl or alkoxy; and the catalyst is selected from a ruthenium compound, a molybdenum compound and an osmium compound.

42. A method according to claim 41 wherein step (c) occurs at room temperature.

43. A method according to claim 1 wherein step (a) comprises applying a ruthenium catalyst in a liquid carrier to the first substrate surface, step (b) comprises applying a metathesizable liquid norbornene monomer to the second substrate surface and step (c) comprises contacting the catalyst-applied first substrate surface and the monomer-applied second substrate surface.
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